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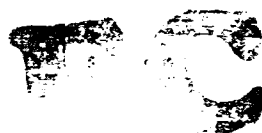
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HEAT RESISTANT EXPLOSIVES IV

A PATENTED NITRATION PROCEDURE FOR THE CONVERSION OF 4 - NITROANILINE
TO 2, 3, 4, 6 - TETRANITROANILINE (C)



30 DECEMBER 1958

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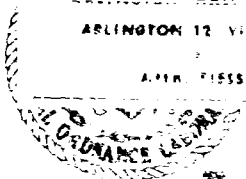
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HEAT RESISTANT EXPLOSIVES IV

A rapid Nitration Procedure for the Conversion
of m-Nitroaniline to 2,3,4,6-Tetranitroaniline

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ABSTRACT: It has been previously demonstrated (1,2) that 2,3,4,6-tetranitroaniline (TNA) can be converted in good yield to 1,3-diazine-2,4,6-trinitrobenzene (DATE). The results of this investigation describe a new semi-continuous batch method and a continuous method for the production of TNA. This procedure has a constant, controllable exotherm and does not exhibit the "flashes-of-fire" or "fuse-offs" observed with previous methods used for the preparation of TNA.

This new method involves the nitration of m-nitroaniline at considerably higher temperatures than used previously. (1,2,4,5). These procedures in the laboratory with a 5-liter flask have produced 2,3,4,6-tetranitroaniline much faster than semi-pilot scale, in a ten gallon kettle, nitrations by the previous low temperature method.

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30 December 1938

This report describes a major improvement in the process for preparing 2,3,4,6-tetranitroaniline, TNA, in large scale production.

The value of facile TNA preparation lies in the fact that it is the intermediate used in the production of INTR, a remarkably heat resistant explosive roughly equivalent to TNT in performance. This work was performed under Task 301-624/42006/03, Explosives Applied Research.

MELL A. PETERSON
Captain, USN
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Albert Lightbody
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By direction

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HEAT RESISTANT EXPLOSIVES IV

A Rapid Nitration Procedure for the Conversion
of m-Nitroaniline to 2,3,4,6-Tetranitroaniline

INTRODUCTION

Recent studies carried out in these laboratories (1) have shown that 1,3-diamino-2,4,6-trinitrobenzene, DATB, is suitable for use as an explosive at temperatures above 250°C. It has been demonstrated previously (1,2) that 2,3,4,6-tetranitroaniline, TNA, can be converted in good yield to DATB. The preparation of TNA, however, was hampered somewhat by a considerable exotherm and brilliant flashes of fire at the surface of the reaction mixture (1,3). Indeed, these flashes of fire were in some cases followed by a "run-off" of the reaction mixture. Hence, the nitration of m-nitroaniline to TNA under the conditions described previously (3) was a difficult procedure, and could become quite dangerous if carried out on a large scale.

A study of the nitration conditions carried out at this laboratory (4) showed that not only could the flashes of fire be eliminated, but also that the exotherm experienced during the reaction could be controlled. This was effected by slowly adding the required amount of 10% nitric acid to a m-nitroaniline-sulfuric acid-sulfur mixture at 20 to 25° and then allowing the mixture to age at this temperature for one to two hours. Subsequent elevation of the temperature, as required in the latter stages of the reaction, did not produce an exotherm which could not be easily controlled on a laboratory scale.

This procedure was very satisfactory when carried out on a laboratory scale. However, it was found that on translating this procedure to the pilot plant, a longer aging time was necessary after the addition of the nitric acid in order to prevent the exotherm from becoming uncontrollable during the heating cycle. Because of this additional aging time only about four pounds of TNA could be made during an eight hour period in a ten gallon reactor. The rate of TNA production was therefore the controlling factor in DATB production.

An investigation of the nitration procedure was undertaken in an attempt to reduce the overall reaction time. Previous studies of the nitration of m-nitroaniline showed that when the nitration was carried out at temperatures of 20 to 25°, an intermediate product separated from the reaction mixture (1,3) as a flocculent gummy precipitate. This material was soluble

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in water, with subsequent decomposition, and was obviously not TNA or a partially nitrated aniline. From previous studies concerning the nitration of aromatic amines, it has been shown that nitramine intermediates are formed in the reaction (6). These N-nitro derivatives undergo a rearrangement to yield the C-nitro derivative in the presence of the acidic nitrating medium.

It seemed reasonable to assume that the nitration of N-nitroaniline to TNA occurs by C-nitration together with N-nitration, followed by rearrangement of the N-nitro derivative to the C-nitro derivative. Hence the intermediate that separates from the low temperature nitration of N-nitroaniline is most probably a polynitro-N-nitroaniline which undergoes rearrangement during the heating cycle to yield TNA. The exotherm observed during the initial stages of the heating cycle when TNA separates from the reaction mixture is therefore probably due to the rearrangement of the polynitro-N-nitroaniline to TNA.

It is now understandable why the temperature rise during the initial stages of the heating cycle can be large and rapid, if care is not taken to remove the excess heat as fast as it is liberated. In a one mole run, for example, practically all of the N-nitroaniline is converted to the polynitro-N-nitroaniline during the low temperature aging period. Since the rearrangement of this intermediate to TNA occurs rapidly, as evidenced by the rate of precipitation of TNA from the reaction mixture during the heating cycle, most of the heat of reaction for this rearrangement is liberated during the early stages of the heating. This sudden liberation of heat gives rise to the large exotherm observed.

As a result of these conclusions, it was decided that the best way to control this exotherm, without sacrificing time, was to effect the nitration of N-nitroaniline in such a manner that only a small amount of the polynitro-N-nitroaniline intermediate would be present in the reaction mixture at any given time. The initial experiments in this investigation were designed with two assumptions in mind:

1. The formation of the intermediate nitramine occurs rapidly at ambient temperatures, and its rate of formation at elevated temperatures would increase in the normal manner.
2. The temperature coefficient of the rate of the rearrangement of the polynitro-N-nitroaniline to TNA is considerably larger than the temperature coefficient of the rate of its

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formation. In other words, although the rate of formation of the nitracine intermediate is much faster than its rate of rearrangement to PNA at ambient temperatures, at elevated temperatures the rate of rearrangement may become equal to or greater than its rate of formation.

If the above assumptions are correct, it should be possible to select a reaction temperature at which one would achieve essentially a "steady state concentration" of the nitracine intermediate which would rearrange to yield PNA as fast as it is formed.

In an attempt to reduce the heat evolved during the nitration reaction still further, the order of addition of reagents in previous work (1) was considered. In these experiments (1) about 0.5 parts of 90% nitric acid were added to a cooled solution of m-nitroaniline (25 to 25°) in one part of 30% oleum and 2.5 parts of concentrated sulfuric acid. This is essentially the same as adding 90% nitric acid to 12% oleum, if one ignores the nitration reaction. During such an addition, considerable heat will be liberated due to the solution of the water present in the nitric acid in the oleum-sulfuric acid mixture. While this order of addition seemed quite suitable for a low temperature reaction, it was felt that the additional heat liberated on mixing reagents would make the reaction temperature more difficult to control in a high temperature nitration. For this reason, all of the experiments described in this work were carried out by premixing the oleum and nitric acid and adding this to a solution of m-nitroaniline in concentrated sulfuric acid.

The final modification to be made was that of the reaction vessel. It was desirable to have a reaction flask in which the reactants could be heated to a specific temperature at the beginning of the reaction. At the same time, however, it was also necessary to use the heating mechanism as a coolant when the exotherm, if any, appeared. For this purpose a jacketed flask was selected, through which a rapid current of hot water could be run. The water would not only serve to heat the reactants during the initial stages of the reaction, but would also act to some degree as a coolant. In addition to the water jacket, the flask was equipped with a drain for removing the contents at the end of a given run. In the case where continuous runs were carried out, this drain enabled the withdrawal of reacted materials, while reactants were being added.

DISCUSSION OF RESULTS

Preliminary runs were made by adding a solution of one part of 90% nitric acid in 2.5 parts 30% oleum to a solution of m-nitroaniline in concentrated sulfuric acid at 55°. At the end of one minute the temperature reached a maximum value of about 80°. TNA began to separate from the reaction mixture almost immediately after the addition of the nitric acid-oleum mixture was completed. At the end of an eight minute reaction period the reaction mixture was drowned and the product isolated. Eight repetitive runs showed that the maximum reaction temperature, due to the exotherm, varied between 75° and 87°. The yield of TNA from eight such runs (63%) compared favorably with that obtained previously (1).

Subsequent runs were made to determine the influence of total pot volume on the maximum temperature reached during the reaction. A two and one-half fold increase in the pot volume caused the maximum temperature achieved to rise to between 98° and 105°, but there was no evidence of decomposition reaction occurring simultaneously with the desired nitration reaction. The yield of TNA from the higher temperature runs was identical with that obtained previously, even though the reaction period was shortened to four minutes.

Since the reaction seemed to be quite controllable, an attempt was made to force the reaction mixture to "hang-off". The quantities of reactants were increased until the pot volume was five times that of the initial runs. Seven runs were carried out in this manner with a four minute reaction time. Although the maximum reaction temperature, due to the exotherm, varied between 102° and 131°, there was no evidence of the "flash of fire" (1,3) or "fuming off" of the reaction mixture. The yield of TNA (51%) was somewhat reduced. It was concluded from this result that TNA in the presence of the nitrating medium underwent a decomposition reaction. However, this reaction does not compete noticeably with the desired nitration reaction until the temperature approaches 120°.

To study the effect of reducing the volume of oleum on the yield of TNA, fifteen runs were carried out with only enough oleum to convert the 90% nitric acid to 100% nitric acid. Thirteen of these runs reached a maximum temperature of 125° to 133° at the end of one and one-half minutes. These runs were kept in the reaction pot for about four minutes. The fourteenth

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run was carried out by doubling the pot volume. In this instance the reaction temperature rose from 55° to 200° within one minute after the addition of the nitrating acid. Although there was considerable evolution of nitrogen dioxide, no evidence of "flashes of fire" or fume off of product appeared. The nitrogen dioxide appeared to come from the decomposition of the nitrating medium and not from decomposition of the product.

The reaction mixture in this run did not yield TNA, but instead a dark, blood-red solution was obtained. The TNA initially formed in this reaction went into solution as the temperature approached 150°. The fifteenth run, carried out on a slightly reduced scale, reached a maximum temperature of 145°. In this instance, the evolution of nitrogen dioxide was considerably reduced. However, once again the TNA formed early in the reaction went back into solution yielding a dark, blood-red reaction mixture. The overall yield of TNA, corrected for the material lost in the last two runs, was identical (52%) with that obtained from 122°-131° runs where the quantity of oleum was not reduced.

The results of the above runs showed that even though the reaction mixture reached a maximum temperature of 200°, there was no danger of explosion or fire due to the presence of large amounts of the polynitro-m-nitro aniline. Indeed, the amount of this intermediate present at any given time during the reaction must be vanishingly small. In addition the results also supported the conclusion that the main factor controlling the yield of TNA is the reaction temperature. At temperatures of about 120° or higher the reaction of the TNA formed with nitrating medium tends to reduce the yield considerably.

The effect of the length of reaction time on the yield was not studied thoroughly. However, the scanty results obtained seemed to show that the reaction time could certainly be reduced from four to two minutes or even less. Certainly reducing the reaction time from eight to four minutes had no effect on the yield of TNA obtained. With this in mind, a study was undertaken to determine whether or not this high temperature nitration method could be converted to a continuous process.

The method used was to build up gradually to a volume of 1.5 liters of reacted material in a five liter reactor by means of the batch process. Once this volume was attained, additional reactants were added at such a rate that the temperature was maintained between 70° and 85°. Reacted material was withdrawn

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at such a rate that the pot volume was kept between 2.5 and three liters. In this manner the total time required for the processing of the same quantity of material as was used in the batch process was halved. The yield of TNA from such a continuous run was increased to 70%, and the production rate, excluding the filtering and drying operation, was 2.1 pounds of TNA per hour. By comparison, a ten gallon reactor operating with the low temperature method (1) can produce four pounds of TNA in six hours.

A second continuous run was carried out using one half the usual quantity of concentrated sulfuric acid for preparing the *m*-nitroaniline solution. It was hoped that the reaction could be controllable under these conditions, since with a smaller volume of solution the same quantity of *m*-nitroaniline could be nitrated in less time. The results proved this point. Under these conditions, the same quantity of *m*-nitroaniline was processed in about three-fourths the time. The yield of TNA from this run (58%) was essentially identical with that obtained from the previous continuous run. In addition, no greater difficulty was experienced in maintaining the reaction temperature between 70° and 80°, even though the volume of sulfuric acid was reduced.

SUMMARY

As a result of this investigation, a process for the preparation of 2,3,4,6-tetranitroaniline has been developed which involves the nitration of *m*-nitroaniline at elevated temperatures with a mixture of nitric acid, oleum and sulfuric acid. Compared to existing methods, this new method is advantageous since it is in no way hazardous and in addition allows one to produce more TNA in a unit time. The method can be adapted to either a continuous process or a batch process.

The results described in the body of the report are not meant to restrict variations in the parameters of quantity of nitrating medium, reaction time, or composition of the nitrating medium. However, one restriction is made; that being the minimum temperature required prior to the addition of the nitrating acid to the same sulfuric solution. In order to prevent the build up of the polymerized-*m*-nitroaniline intermediate in the reaction mixture, it is essential that the temperature of the same sulfuric solution at the start of the reaction be at least 50° to 55°.

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EXPERIMENTAL

Nitration of m-Nitroaniline, Batch Method. The following solutions were prepared:

1. One mole (137 g) of m-nitroaniline was dissolved in 1.2 liters of concentrated sulfuric acid. The mixture was stirred during the solution, but it was not necessary to cool the acid during the addition of the amine.

2. With cooling in ice and stirring, 480 cc of 30% oleum were added to 270 cc of 90% nitric acid. The temperature was not allowed to rise above 70° during the addition.

Nitration. A two-liter, three-necked, water jacketed flask was fitted with a stirrer and a glass adapter containing a dropping funnel and thermometer. The third neck was fitted with a standard taper solids addition funnel. Tap water at 60° was run through the water jacket as rapidly as possible.

One hundred and sixty cubic centimeters of the m-nitroaniline-sulfuric acid solution were introduced into the flask, and the stirrer started. When the temperature of the contents had reached 35° to 40°, 30 cc of the oleum-nitric acid mixture was added as rapidly as possible through the dropping funnel. The temperature began to rise almost immediately and the mixture turned red-brown. After about two minutes, a yellow solid began to precipitate and the temperature started to fall from its maximum. At the end of an eight minute period, the mixture was withdrawn from the flask by means of a stopcock sealed through the water jacket, and drowned in ice.

The combined drowned product from all the runs was filtered with caution, washed with water till no longer acid to pH paper, and dried in vacuo at 60°. The yield of TNA was 130 grams (85% corrected for first run which was lost; see data table); m.p. 205°-207°.

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Run	t_r , °C	t_{max} , °C	Time to reach t_{max} , min.	t_{cool} , °C
1	55	75	1.0	55/2
2	55	75	1.5	60
3	56	77	1.5	55
4	58	78	1.0	62
5	55	65	1.0	63
6	60	87	1.5	62
7	57	87	1.5	60
8	60	90	2.0	62/2

4. This run was lost during the draining procedure.

5. Remainder of stock solutions used in this run: 180 cc of amino-sulfuric acid and 90 cc of oleum-nitric acid mixture.

Nitration of m-Nitroaniline, Batch Method. The following solutions were prepared:

1. Five moles (690 g) of m-nitroaniline were dissolved in 624 liters of concentrated sulfuric acid as described previously.

2. To 1.05 liters of 90% nitric acid was added 2.4 liters of 70% oleum at such a rate that the temperature did not rise above 60°. The mixture was cooled in ice during the addition.

Nitration. The nitration procedure was identical with that described in the previous runs with the exception of the following modifications:

1. A five liter jacketed reactor was used.

2. The reaction cycle was four minutes.

The exact quantities of reactants per batch and reaction temperatures are completely described in the following table:

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Run	NH ₄ ⁺ /mixed acid/a	t°, °C	t _{max} , °C	Time to reach t _{max} , min.
1	400/200	58	115	2.0
2	400/200	58	115	2.0
3	400/200	56	105	2.0
4	400/200	56	106	2.0
5	400/200	56	104	2.0
6	400/200	56	98	2.0
7	400/200	56	97	2.0
8	400/200	56	101	2.0
9	400/200	56	99	2.0
10	400/200	56	104	2.0
11	400/200	56	101	2.0
12	400/200	56	105	2.0
13	400/200	56	102	2.0
14	800/400	56	130	2.0
15	800/200	56	122	2.0

/a. Gc of saline sulfate solution/cc of mixed acid.

The product was crowned and worked up as described in the previous run. The yield of THA was 860 grams (53%); m.p. 206°-209°.

Nitration of m-Nitroaniline, Batch Method with Improved Pot Volume. The stock solutions of reactants were prepared with the identical quantities as in the above run. A five liter reactor was used, with a reaction cycle of four minutes. The results of this run are summarized in the following table:

Run	NH ₄ ⁺ /mixed acid/a	t°, °C	t _{max} , °C	Time to reach t _{max} , min.
1	400/200	55	93	2.0
2	500/200	56	110	2.0
3	800/400	53	120	2.0
4	800/400	54	128	2.0
5	800/400	55	125	2.5
6	800/400	56	126	2.0
7	800/400	51	122	2.0
8	800/400	57	131	2.0
9	800/325	51	107	2.0

/a. Gc of saline sulfate solution/cc of mixed acid.

The product was crowned and worked up as described in the previous run. The yield of THA was 895 grams (53%); m.p. 205°-207°.

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Nitration of m-Nitroaniline, Batch Method, Stoichiometric Glass.
The following stock solutions were prepared:

1. Five moles (690 g) of m-nitroaniline were dissolved in six liters of concentrated sulfuric acid as described previously.

2. To 1.05 liters of 90% nitric acid was added 1.19 liters of 30% oleum at such a rate that the temperature did not rise above 60°. The mixture was cooled in ice during the addition.

Nitration. The nitration procedure was identical with that described in the previous run, except for the fact that a 3.5 minute reaction cycle was used. The exact quantities of reagents per batch and reaction temperatures are completely described in the following table:

Run	mls./mixed acid/c	50° °C	t _{max} °C	Time to reach t _{max} , min.
1	400/125	55	130	1.5
2	400/125	55	125	2.0
3	400/125	55	125	1.5
4	400/125	55	121	1.5
5	400/125	55	121	1.5
6	400/125	55	128	1.0
7	400/125	53	122	1.0
8	400/125	54	123	1.0
9	400/125	55	130	1.5
10	400/125	54	123	1.0
11	400/125	54	133	1.0
12	400/125	55	132	1.0
13	400/125	54	153	1.0
14	800/250	51	200	0.5-1.0 ^{1/2}
15	400/125	54	145	1.0 ^{1/2}

/a. The temperature rapidly rose to 130° with a slight evolution of nitrogen dioxide. Some TNA precipitated during this period. Instead of the temperature peaking as in the other runs, it continued to rise at a very rapid rate reaching a maximum of 200°. During the latter portion of the temperature rise, considerable evolution of nitrogen dioxide occurred with some of the TNA still present being spewed out the neck of the flask by the gas stream. THERE WAS NO EVIDENCE OF FLASHING OR VIOLENT DECOMPOSITION OF TNA EVEN AT 200°. At the 140°-150° mark the TNA went back into solution and the reaction mixture turned dark red. On crowning this batch, a dark red solid separated. No further work was done with this material, although it could be m-nitrotetranitro-aniline.

/b. TNA started to precipitate from this reaction mixture as the temperature rose to t_{max}. At the 130°-140° mark, the precipitated TNA went back into solution yielding a dark red reaction mixture as in run 14.

/c. Cc of amine sulfate solution/cc of mixed acid.

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The product was drowned and worked up as in the previous runs. The yield of TNA was 601 grams (52%, corrected for runs 14 and 15 in which no product was obtained); m.p. 204°-207°.

Nitration of m-Nitroaniline, Continuous Method. The following stock solutions were prepared:

A. Five moles (690 g) of m-nitroaniline were dissolved in six liters of concentrated sulfuric acid as described previously.

B. One and five hundredths liters of 90% nitric acid and 2.4 liters of 30% oleum were mixed as described previously.

Nitration. In a five-liter water jacketed reactor was placed 400 cc of stock solution A. The temperature was raised to about 50°-55° by passing a rapid stream of 60° water through the water jacket. At this point, 200 cc of stock solution B was added as rapidly as possible with vigorous stirring. The temperature of the reactants rose to about 100° within a two minute period, and then dropped off rapidly to 65°. When this temperature was reached, 400 cc of solution A and 200 cc of solution B were added to the reactor simultaneously, without withdrawing the already reacted material. After this addition, the temperature reached a maximum of only 85°. After the temperature had returned to 65°-70°, solutions A and B were added to the mixture simultaneously from graduated dropping funnels in the ratio A/B = 2/1. The rate of addition was such that the temperature was maintained between 70° and 80° by the heat of reaction and the passage of 60° water through the jacket of the reactor.

When the total volume of reactants in the reactor had reached 2500 to 3000 cc, the addition was stopped and the contents of the flask were reduced to about 1500 cc by withdrawing reacted material through the stopcock drain in the bottom of the flask. During the withdrawal, the mixture was stirred continuously so as to remove a homogeneous mixture. The material withdrawn was drowned in ice and the precipitated TNA was filtered with suction, washed with water till the washings were neutral to pH paper, and dried in vacuo at 60°.

After the volume of reacted material was reduced to 1500 cc, the addition of solutions A and B was again commenced in a manner similar to that described above. In this way, it was possible to react the total volume of solutions A and B prepared in about one hour. The yield of TNA obtained from this run was 945 grams (70%); m.p. 209°-210°.

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Nitration of m-Nitroaniline, Continuous Method, Reduced Sulfuric Acid. The following solutions were prepared:

A. Five toles (690 g) of m-nitroaniline were dissolved in three liters of concentrated sulfuric acid.

B. One and five hundredths liter of 90% acid and 2.4 liters of 30% oleum were mixed as described previously.

Nitration. The procedure followed was identical with that described in the previous continuous run with the following exception:

The ratio of the volumes of solutions A and B added at any time during the reaction was $A/B = 1/1$. The ratio was changed in this manner since the total volume of solution A in this run was essentially one-half of what it was in the previous run.

The total volume of solutions A and B were processed in about three-quarters of an hour, yielding after a similar work up, 925 grams (68%) of m-TNA; m.p. 206° - 208° .

ACKNOWLEDGMENT

The assistance of Mr. Francis Taylor, Jr. in carrying out some of the experiments mentioned herein was greatly appreciated.

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